Local vibrational modes in Mg-doped GaN as a probe of activation and deactivation of acceptors

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As-grown Mg-doped GaN films prepared by metalorganic chemical vapor deposition (MOCVD) show high resistivity when H_2 carrier gas is used in the growth process. To get p-type conductivity, low-energy electron beam irradiation [1] or thermal annealing in N_2 ambiance [2] is necessary. A plausible explanation is that H atoms are passivating Mg acceptors [2]: Namely, H impurities in as-grown films are bonded as positive ions to Mg in Ga site. By annealing in N_2 ambiance, H atoms leave Mg and p-type conductivity is obtained. When p-type conductive films are exposed to NH_3 gas, on the contrary, films show again highly resistivity [2]. This may be also explained by this passivation model. A good method to verify this picture is to observe related local vibrational modes (LVM) by IR absorption or Raman scattering. Since H atoms are lighter than any other species, and Mg atoms have smaller mass than the host atom Ga, it is well expected that related LVMs are observed in the spectra. Actually, LVM related to Mg-N-H bonding was observed recently in as-grown films [3] [4] and its variation in the N_2-annealing process [4] gave a supporting evidence of this picture. In the present work, LVMs in Mg-doped GaN films are investigated by Raman scattering with focus on the variation by annealing in N_2- and NH_3-ambiance. We will clarify the behavior of H impurities in the activation and deactivation process of Mg.

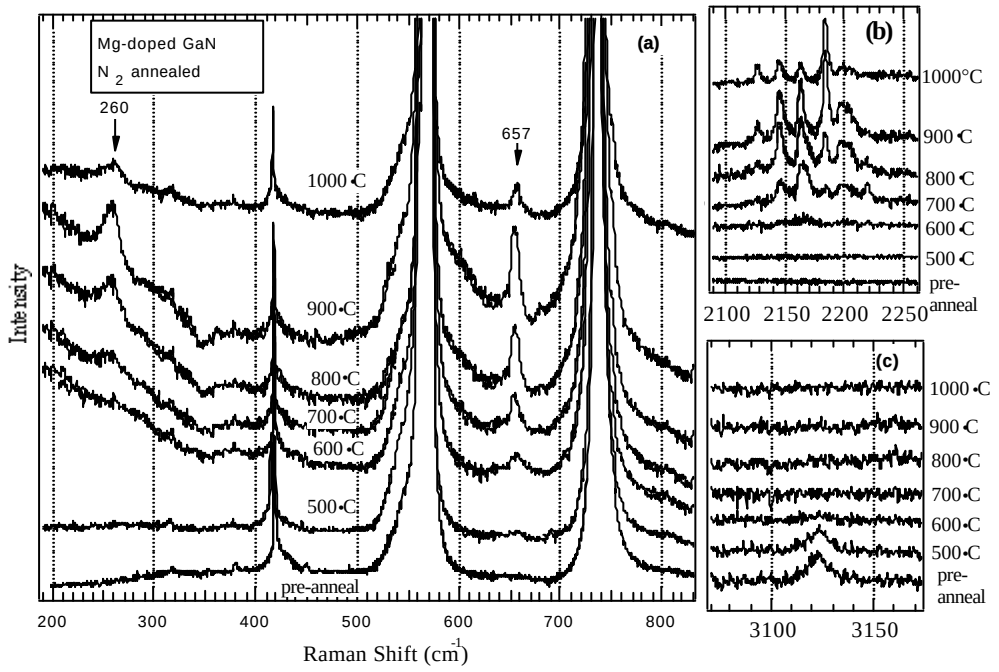

Fig. 1
Raman spectra of Mg-doped GaN films after annealing in N_2 ambiance at various temperatures. (a) to (c) denote different spectral regions. The intense peaks in (a) are phonon bands of GaN (568, 735 cm^{-1}) and sapphire substrate (418 cm^{-1}).

At first, we examined Mg-doped GaN films grown by MOCVD with post-annealing at various temperatures in 500-1000°C in N_2 ambiance. **Figure 1** shows the result. Here, (a) to (c) denote different frequency regions. The sharp strong signals in (a) are assigned to phonon bands of GaN, namely, E_2 mode at 568 cm^{-1} and A_1 (LO) mode at 735 cm^{-1}, and that of the sapphire substrate at 418 cm^{-1}. When the temperature was higher than 600°C, LVMs assigned to Mg-N bonding appeared at 657 and 260 cm^{-1} as shown in (a), LVM for Mg-N-H complex at ~3120 cm^{-1} [3] in (c) disappeared, and instead, H-related LVMs newly appeared at 2100-2250 cm^{-1} in (b). A low-frequency continuum band, which is ascribed to the inter-valence band transition of hole, also appeared at above 600°C at <~400 cm^{-1} as shown in (a). These results indicate that H atoms first bonded to Mg in as-grown films are liberated at above 600°C and Mg

atoms are activated. The H atoms may desorb the films, or rest in the films to form new chemical bondings with some partners such as Ga or some vacancies giving LVMs at 2100-2250 cm^{-1}. This is shown schematically in **Fig.2**. These features were clearly observed up to ~900°C, but weakened at ~1000°C [4].

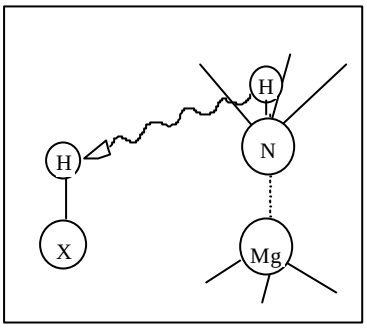

Fig.2 Schematic representation for the activation process of Mg acceptors in GaN by annealing in N_2 ambiance.

Next, Mg-activated, low-resistive samples were annealed at various temperatures at 500-1000°C in NH_3 ambiance. **Figure 3** shows representative Raman spectra. Here, (a) and (b) show the lower- and higher-frequency regions, respectively. The spectra after annealing in 400 or 500°C retain typical characteristics of p-type conductivity as observed in Fig.1 for samples after N_2-annealing at 700-900°C. Noticeable change occurred at above 700°C of annealing; First, the low-frequency continuum band in (a) clearly decreased in intensity. It finally disappeared at 800°C. Attenuation of this inter-valence band transition means that the p-type conductivity is lost, i.e., the advent of highly resisitvity. This is consistent with a previous Hall-effect study [2]. LVMs related to Mg-N bonding at 260 and 657 cm^{-1} also decreased in intensity at above 700°C. These results suggests that H atoms derived from decomposed NH_3 interfere with activation of Mg. Behavior of H atoms can be discussed more clearly by observing the higher-frequency region as shown in Fig.3 (b); After annealing at 800°C, H-related LVMs at 2100-2250 cm^{-1} sharply peaked after 400°C annealing grew in intensity and were heavily broadened. A new broad and intense band also appeared at around ~3000cm^{-1}. These features indicate that the H atoms incorporated in the annealing process form various combinations of LVM; Possible partners will be, e.g., Ga, Mg, their complexes [5] or some vacancies. They will appear at around 2100-2250 cm^{-1} as speculated in the annealing process in N_2-ambiance. High density of incorporated H atoms resulted in the severely broadened features. The appearance of the broad band at ~3000cm^{-1} suggests that H atoms are also incorporated in the neighborhood of the Mg-N bond. The H atoms will occupy various inequivalent sites including the one shown in Fig.2, and passivate Mg acceptors.

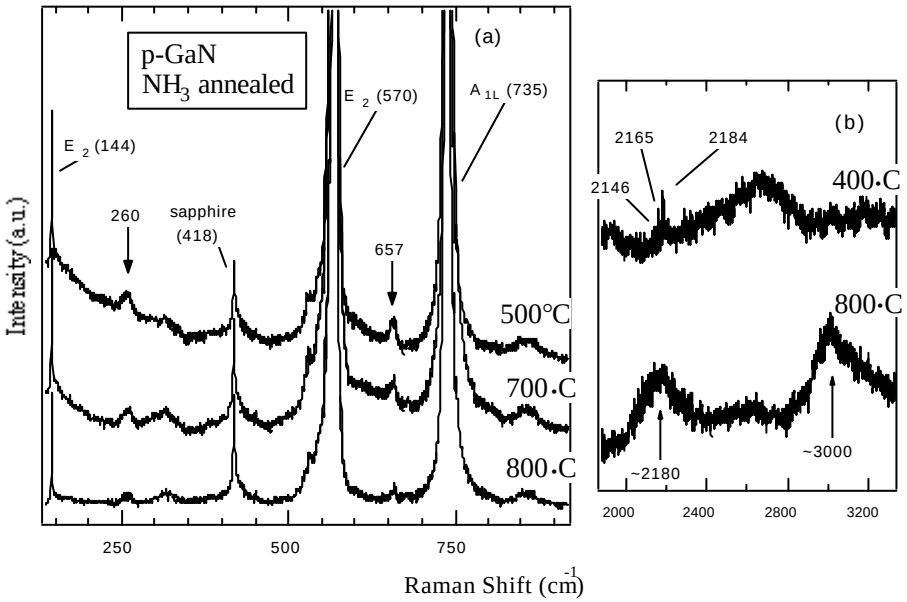

Fig.3 Raman spectra of Mg-doped p-typeGaN films after annealing in NH_3 ambiance at different temperatures. The intense peaks are phonon bands of GaN and the sapphire substrate.

References

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